METHYLATION OF ETHYLENE OVER LEWIS-ACID CATALYSTS

M.V.C. Sekhar

Energy Research Laboratories, CANMET, Natural Resources Canada, 555 Booth Street, Ottawa, Canada, K1A 0G1
email:sekhar@emr.ca

Keywords: Alkylation, Lewis-acids, Methane conversion

INTRODUCTION

As a major constituent of natural gas, methane is abundant and is a relatively inexpensive feedstock for a variety of chemicals. The use of methane as a fuel is straightforward. Consequently, over the years, considerable research has been conducted to develop technologies for its efficient utilization. Work[1] on adsorbents for storing natural gas on-board automotive vehicles promises to expand its use considerably. Conversely, the use of methane as a chemical feedstock requires either the energy- and capital-intensive production of intermediate synthesis gas or its thermal cracking to a range of hydrocarbons. In recent years there has been a great deal of interest in processes[2-4] that convert methane directly to olefins, methanol and other functionalized methane derivatives.

Among the various conversion processes currently under development, the Oxidative Coupling (OC) route is the most promising. With increased attention being given to OC process, engineers have also begun outlining the corresponding reaction engineering aspects. The OC of methane rich natural gas yields a dilute olefin stream. At 25% hydrocarbon conversion, the ethylene in the dry reactor effluent is about 5%, with some propylene and other hydrocarbons. Because of the presence of large amounts of unconverted methane in the effluent, product separation is one of the main points of optimization in the existing oxidative coupling technology. Consequently, a processing scheme which does not require further separation of the product of the OC rector would be of considerable advantage. Reactions between methane and ethylene using a number of solid acids have also been reported by a number of authors[5-7] in the past. However, some of these experiments were conducted at temperatures higher than ambient. In this paper we report some of the results obtained at ambient temperature as part of a screening program for developing catalyst systems for co-reacting methane with ethylene to produce higher hydrocarbons.
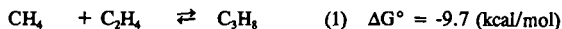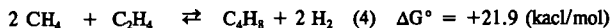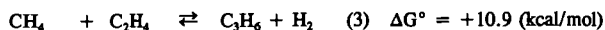
PROCEDURES

Catalyst preparation. The catalyst that was most extensively tested was a mixture of NbF_5 and AlF_3. The catalysts were prepared using anhydrous hydrogen fluoride as a solvent. The metal fluorides were first physically mixed and then dissolved in anhydrous hydrogen fluoride. The mixture was stirred for about an hour, then the excess HF was allowed to evaporate by heating the mixture to about 100°C for several hours.

Experimental conditions. All experiments were carried out in a continuous flow fixed bed micro-reactor with a catalyst volume of between 5 and 10 mL. Experiments were conducted at two pressures, ambient and 10 atm. On line chromatography was used for product analysis. Samples were also collected and analyzed by off-line GC-MS. Experiments were preformed with two different ratios of methane and ethylene. Nitrogen was used a tracer in several experiments in order to obtain a quantitative measure of the conversions. The catalysts were used in the form of fine powders and was diluted with dried sand or teflon chips.

RESULTS AND DISCUSSION

A number of reactions between methane and ethylene and other olefins are thermodynamically favoured even at ambient temperature, provided the products are alkanes, viz., (reactions 1 and 2)

$$CH_4 \ + \ C_2H_4 \ \rightleftarrows \ C_3H_8 \qquad (1) \quad \Delta G° = -9.7 \ (kcal/mol)$$

$$CH_4 \ + \ C_3H_6 \ \rightleftarrows \ C_4H_{10} \qquad (2) \quad \Delta G° = -4.5 \ (kcal/mol)$$

$$CH_4 \quad + \quad C_2H_4 \quad \rightleftarrows \quad C_3H_6 + H_2 \quad (3) \quad \Delta G^\circ = +10.9 \text{ (kcal/mol)}$$

$$2\,CH_4 \quad + \quad C_2H_4 \quad \rightleftarrows \quad C_4H_8 + 2\,H_2 \quad (4) \quad \Delta G^\circ = +21.9 \text{ (kacl/mol)}$$

The formation of unsaturates (reactions 3 and 4) are associated with positive free energy change at ambient temperature. Self-oligomerization of ethylene to alkenes, however, is thermodynamically feasible:

$$2\,C_2H_4 \quad \rightleftarrows \quad i\text{-}C_4H_8 \text{ etc. } (5) \qquad \Delta G^\circ = -18.7 \text{ (kcal/mol)}$$
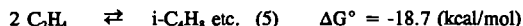
Table 1 compares the ethylene conversions obtained for reaction between ethylene and methane for two different methane/ethylene feed ratios. The corresponding product distributions, excluding unreacted methane and ethylene are shown in Table 2. Using a 7:1 molar ratio of methane to ethylene, almost complete conversion of ethylene is obtained, whereas at a higher ethylene content in the feed, conversions are reduced by half. The ethylene conversions continue to remain higher when the feedstream is richer with respect to methane. The presence of C_5 hydrocarbons, n-pentane and 2-methyl butane, along with traces of propane suggests the participation of methane in the reaction sequence, since oligomerization of ethylene alone should yield even numbered unsaturated hydrocarbons. However, the methane conversions in these experiments were less than what would be expected based on the primary alkylation reaction (reaction 1), suggesting a larger contribution from oligomerization. The absence of olefins in the product spectrum resulting from such oligomerization is probably due to secondary reactions.

When ethylene alone was used as a reactant, the conversions of ethylene are much lower than when methane was also present in the feed mixture (Table 3). The product spectrum in the case of ethylene only experiments, is qualitatively similar to the case where methane was also present, however, the product is relatively richer in heavier hydrocarbons (Table 4). Small amounts of methane was also detected when ethylene alone was used as a feed, indicating that cracking of heavier hydrocarbons had occurred under these experimental conditions. The cracking also could explain the observation of negative methane conversions in some experiments. The absence of propane and butenes could be explained by the following reaction sequences. Propane which is formed by the primary alkylation reaction (reaction 1), undergoes ethylation with ethylene to produce a C_5 alkane (reaction 6).

$$C_2H_4 + C_3H_8 \quad \rightleftarrows \quad C_5H_{12} \quad (6)$$
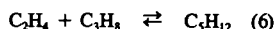
Oligomerization of ethylene produces butenes (reaction 5) as intermediates, which are alkylated by methane, also producing C_5 hydrocarbons (reaction 7). A similar reaction involving the alkylation of isobutane by ethylene was recently reported[8], producing mainly hexanes in addition to a variety of other alkanes and alkenes formed by secondary reactions.

$$CH_4 + C_4H_8 \quad \rightleftarrows \quad C_5H_{12} \quad (7)$$

By far the most abundant C_5 hydrocarbon detected was isopentane and its formation can be explained by both of the above reactions. The formation of isobutane as the most abundant hydrocarbon product suggests extensive cracking of the C_5 and C_6 species (reaction 8).

$$C_5H_{12} \quad \rightleftarrows \quad i\,C_4H_{10} + CH_x \quad (8)$$

The CH_x species could then be hydrogenated to methane by abstracting hydrogen from residual HF that was used in the preparation of the catalyst. Such cracking followed by hydrogenation could also explain the negative conversions of methane that was observed in a number of instances.

In order to discern the extent of the incorporation of methane in the reaction product, an experiment was performed using $^{13}CH_4$ and unlabelled ethylene. The products were collected and analyzed off-line using a Porapak Q column and a mass selective detector. The mass spectrum of isobutane form reactions using labelled and unlabelled methane were then compared.

By measuring the abundance of the parent ions it was possible to quantify the amount of labelled isobutane present in the sample. From these data it was concluded that there was incorporation of at least one labelled carbon in the C_4 skeleton and it was estimated that 5% of the total isobutane formed contained the labelled ^{13}C. By comparison, the methane conversion for the same set of experiments was about 9%. This discrepancy can arise due to the fact that the formation of isobutane probably involves several alkylation and cracking steps. In such a scenario, the labelled carbon could be lost as either methane or some other hydrocarbon. The presence of labelled carbon in the other products such as 2,2-dimethyl butane or 2,3-dimethyl butane could not be established unambiguously due to the complex mass spectral fragmentation pattern of these compounds. The GC-MS analysis also revealed the formation of traces (about 50 ppm) of two fluorinated hydrocarbons, fluoroethane and 1,1-difluoroethane.

SUMMARY

The catalytic activity of metal fluoride based Lewis acid catalysts for the coreaction between methane and ethylene was studied. It was found that whereas substantial conversion of ethylene could be obtained even at ambient temperatures, methane conversions were much lower. Experiments using labelled methane confirmed the participation of the methane in the reaction sequences. The primary products were branched C_4 and C_5 saturates, with smaller amounts of straight chain hydrocarbons. The activity of the catalyst was found to decrease sharply with time, with the product spectrum shifting towards C_6 and higher hydrocarbons.

ACKNOWLEDGEMENTS

REFERENCES

1. R. Chahine and T.K. Bose, Twentieth Biennial Conference on Carbon, Santa Barbara, June 23-28, 1991.
2. Preprints Amer. Chem. Soc. Division of Petr. Chem., Symposium on Methane and Alkane conversion, 39(2), 1994.
3. C. Mirodatos, J.M. Basset, G.A. Martin and J. Saint-Just, Eds., Catalytic Methane Conversion, Proceedings of the Third European Workshop on Catalytic Methane Conversion, Villeurbanne, France, May 27-29, 1991, Catalysis Today, 13(2-3), 1992.
4. Preprints Amer. Chem. Soc. Division of Petr. Chem., Symposium on Natural gas Upgrading II, 37(1), 1992.
5. G.A. Olah, J.D. Felberg and K. Lammertsma, J. Am. Chem. Soc., 105, 6529 (1983).
6. M.S. Scurrell, Appl. Catal., 34, 109 (1987).
7. F.T.T. Ng, C.R. Rourke and J. Lynn, Progress in Catalysis, K.J. Smith and E.C. Sanford (Eds.,) Elsevier, 1992, p.31.
8. J-M. Goupil, J-L. Poirier and D. Cornet, Ind. Eng. Chem. Res., 33, 712 (1994).

Table 1. Comparison of Ethylene Conversions (mol%) for different feed compositions

Experimental conditions: Catalyst: 1g; Temperature: ambient; Pressure: 10 atm; Total flow: 40 mL/min.

Time(min)	15	45	73	102	158	189	217
Methane/ethylene (3:1)	55.6	13.3	7.17	3.83	2.92	2.01	1.38
Methane/ethylene (7:1)	*94.6*	*71.5*	*36.7*	*11.5*	*4.49*	*3.35*	*3.18*

Table 2. Product composition (mol%) excluding unconverted methane and ethylene.

Experimental conditions: same as in Table 1.
Methane/ Ethylene Mol Ratio: 3:1 (upright data); 7:1 (italics data)

Component / Time(min)	15	45	73	102	158	189	217
Propane	0. 39						
Propane	*0.03*	*0.15*					
isobutane	60.8	74.3	69.4	64.1	61.4	60.3	22.4
isobutane	*76.6*	*61.9*	*58*	*43*	*65.3*	*63.8*	*63*
n-butane	2.79	3.6	4.06	6.5	8.12	8.81	3.49
n-butane	*2.13*	*1.76*	*1.5*	*1.2*	*2.59*	*2.89*	*3.14*
isopentane	16.1	21.8	25.9	28.9	30.5	30.9	11.5
isopentane	*19.2*	*15.6*	*15*	*16*	*32.2*	*33.3*	*33.8*
n-pentane	0.24	0.37	0.67	0.47			
n-pentane	*0.1*	*0.13*	*0.1*	*0*			
C_{6+} hydrocarbons	19.8						62.6
C_{6+} hydrocarbons	*1.88*	*20.4*	*26*	*41*			

Table 3.   Ethylene conversions for ethylene oligomerization vs methane/ethylene coupling

Experimental conditions: Catalyst: 1g; Temperature: ambient; Pressure: 10 atm; Total flow: 120 mL/min.

Time(min)	5	33	62	90	119	219	251
Methane/ethylene (7:1)	93.8	5.34	1.00	1.07	0.71		
Argon/ethylene (7:1)	*76.7*	*23.5*	*5.25*	*3.70*	*3.70*	*2.92*	*2.72*

Table 4. Product composition (mol%) excluding unconverted methane and ethylene.

Experimental conditions: same as in Table 3. With ethylene alone as feed, argon was added to balance the total flow.   Methane/ Ethylene Mol Ratio: 7:1 (upright data); Ethylene alone (italics data)

Component / Time(min)	5	33	62	90	119	219	251
Ethane	*3.25*						
Propane	0.02						
Propane	*0.02*						
isobutane	63.1	26.3	21.0	19.6	18.7		
isobutane	*57.7*	*50.4*	*21.6*	*19.0*		*15.8*	*15.4*
n-butane	2.00	3.44	2.44	2.29	2.36		
n-butane	*4.04*	*2.73*	*2.86*	*2.85*		*3.35*	*3.46*
isopentane	17.4	15.3	13.7	13.4	12.9		
isopentane	*16.2*	*15.6*	*13.4*	*12.7*		*11.6*	*11.6*
n-pentane	0.04	0.80	1.99	0.70	0.60		
n-pentane	*0.04*	*0.06*					
C_{6+} hydrocarbons	17.4	54.2	60.9	64.0	65.4		
C_{6+} hydrocarbons	*18.8*	*31.2*	*62.9*	*65.5*		*69.2*	*69.6*